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<b>(54) Title:</b> GRANULAR CALCIUM CARBONATE FOR USE AS A DIRECT ADDITIVE FOR THERMOPLASTICS  <b>(57) Abstract</b>  A thermoplastic granule containing a high proportion of a particulate carbonate filler in a thermoplastic binder, for blending with an end product thermoplastic in which the carbonate filler is to be dispersed. The granule comprises at least 85 % by weight of a particulate carbonate which is coated with one or more fatty acids having a carbon chain length of from 12 to 20 carbon atoms. The balance of the granule by weight comprises a thermoplastic polymeric binder which is solid at ambient temperature and is compatible with the end product thermoplastic in which the carbonate filler is to be dispersed. The polymeric binder is an amorphous polyolefin and/or a highly branched polyethylene wax. The PSD of the carbonate is selected to maximize packing.		

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GRANULAR CALCIUM CARBONATE FOR USE AS A DIRECT  
ADDITIVE FOR THERMOPLASTICS

FIELD OF INVENTION

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This invention relates generally to mineral fillers for thermoplastics, and more specifically relates to a thermoplastic granule or pellet containing a high proportion of a particulate carbonate filler in a  
10 thermoplastic binder, for blending with an end product thermoplastic in which the carbonate filler is to be dispersed.

BACKGROUND OF INVENTION

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The present invention relates to a particulate product containing a high concentration of an inorganic material, and, in particular, of calcium carbonate, which may be blended with a thermoplastic polymer, such as a  
20 polyolefin. The blend produced will result in a homogeneous, inorganic material filled composite after being processed using conventional methods such as injection molding and extrusion. The invention allows inorganic material filling of thermoplastics to be  
25 achieved without the need for a separate mixing process. The invention provides a means of achieving higher concentrations of inorganic material than has been achievable by prior art without the use of an agent or additive (sometimes referred to in prior art patents as  
30 "fluidifacients") designed to facilitate ease of redispersion.

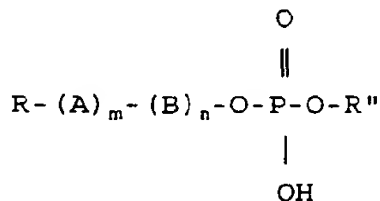
The thermoplastic processing industry has long used inorganic materials as additives for thermoplastic  
35 resins. Introduction of these inorganic materials into the polymer has traditionally been achieved using a number of techniques, including those described below.

a) The polymer, inorganic material and other additives may be subjected to intensive mixing using mechanical systems designed to disperse the inorganic material and additives in the polymer at a temperature above the melting point of the polymer. The proportion of inorganic material and additives in the mixture of polymer, inorganic material and additives is the same as that required in the final product. Suitable mixing equipment includes internal mixers of the Banbury type, twin or single screw extruders and continuous compounders. Once the inorganic material has been dispersed, the melted mixture must be converted into a particulate product form such as granules which will facilitate subsequent processing, e.g. injection molding or extrusion.

b) The polymer, inorganic material and other additives are mixed in a similar way to that described above, except that the inorganic material is first surface treated with a hydrophobic material to render it compatible with organic polymers. Examples of such hydrophobic materials include carboxylic acids of moderate to high molecular weight such as butyric, lauric, oleic and stearic acid, organosilane coupling agents, organotitanates and zircoaluminates. The proportion of inorganic material and other additives in the mixture of polymer, inorganic material and additives is much higher than is required in the final product. Inorganic material concentrations in the order of 75 to 80 weight percent may be produced using this technique. Mixtures with inorganic material contents above this level become both difficult to produce and difficult to redisperse in subsequent processing steps. The final particulate product (e.g. granules) is blended with unfilled thermoplastic polymer immediately prior to entering the final processing operation in such a ratio as to produce a mixture with a lower inorganic material

content which is uniformly distributed and dispersed throughout the system.

c) Highly concentrated, redispersible inorganic material compositions are described in U.S. Patent 4,803,231 which have inorganic material contents in excess of the 75 to 80% by weight achievable using conventional methods. This patent describes a composition which contains three components: (1) a polyolefin polymer or blend of polymers between 19.99 and 4.05 percent of the composition; (2) 80 to 95 percent inorganic material; and (3) an agent which renders the mixture fluid (a fluidifacient) included at 0.01 to 0.95 percent. This fluidifacient is described as an orthophosphoric acid ester with the general formula:



Where A represents ethylene oxide, B represents propylene oxide,  $0 < (m+n) < 24$ , R represents an alkyl group (which may be linear or nonlinear, and may be saturated or unsaturated), an aryl group, or a heterocycle (which may be saturated or unsaturated), wherewith said alkyl, aryl or heterocycle group has 5-28 C atoms, preferably 8-24 C atoms, or R is a steroid group; wherewith further the group R may be branched or unbranched and/or may have one or more functional groups, for example, Halogen, -OH, -COOH, -COOR, -NO<sub>2</sub>, -NH<sub>2</sub>, -CONH<sub>2</sub>, -CN OR OPO<sub>3</sub>H<sub>2</sub>; AND R' may be hydrogen, a carbon chain having 1-4 C atoms, or a group R as defined supra. Thus it is possible that the group R' is identical to the group R.

This composition may be blended with unfilled polymer prior to entering the final processing operation in such

a ratio as to produce a mixture with a lower inorganic material content which is uniformly distributed and dispersed throughout the system. The resultant mixture contains a reduced level of the polyolefin polymer used for preparation of the concentrate as a result of the increased concentration of inorganic material. In discussing this invention in the common assignee's Canadian Patent Application No. 2016447 (the discussion is of equivalent patent EP 0 203 017) it is observed that although a theoretical level of filler of up to 95 percent is disclosed, a practical limit is only 88% by weight of calcium carbonate. In addition, the use of relatively toxic phosphate esters limits the applicability of this system to non-food contact systems.

d) European Patent Application No. 0355808 describes the use of a mixture of a fatty acid salt in combination with a fatty acid amide in the ratios between 10:90 and 90:10 as a coating for calcium carbonate to reduce the surface tension of the inorganic material surface. This coating was also evaluated as a replacement for the orthophosphate ester described in U.S. Patent No. 4,803,231 (described above) with a view to producing a redispersible composite.

e) The aforementioned Canadian Patent Application No. 2016447 describes a process used to produce a redispersible composite which uses a volatile solvent to prepare the product. This solvent and moisture are eliminated, leaving a inorganic material containing a hydrophobic coating in a hydrophobic binding agent. The composition of this product after elimination of solvent and dispersing agent is claimed to be 92.1 - 96.1% inorganic material, 0.1 - 3.0% of a hydrophobic surface coating agent and 3.8- 4.9% of a hydrophobic binder system. This product may be added directly to thermoplastic systems in such proportion as is required

by the final formulation. The reduced binder content allows addition to flame retardant polymer systems without adversely influencing flame retardancy. The volatilization step used in this process tends to  
5 introduce undesirable complexity and costs.

In general, it will therefore be evident from the foregoing that the methods available to date are based either on use of high binder contents and hence introduce  
10 a high binder content into the final polymer composition; or rely on the use of dispersion or fluidifacient additives or agents to allow a highly concentrated inorganic material composite to be produced which will redisperse with ease in thermoplastic polymers.

15

#### SUMMARY OF INVENTION

Now in accordance with the present invention, a thermoplastic granule is provided containing a high  
20 proportion of a particulate carbonate filler in a thermoplastic binder, for blending with an end product thermoplastic in which the carbonate filler is to be dispersed. The granule comprises at least 85% by weight (and preferably 85 to 92% by weight) of a particulate  
25 carbonate which is coated with a fatty acid or blend of fatty acids having a carbon chain length of from 12 to 20 carbon atoms. The balance of the granule by weight is a thermoplastic polymeric binder which is solid at ambient temperature and is compatible with the end product  
30 thermoplastic in which the carbonate filler is to be dispersed. The polymeric binder is selected from one or more members of the group consisting of amorphous polyolefins and highly branched polyethylene waxes.

35 The term "granule" as used herein is intended to refer to the individual discrete components which in total comprise a particulate which as such is in use blended

with the aforementioned end product thermoplastic. These discrete components can have irregular surface characteristics as commonly results from granulation, or can have smooth continuous surfaces as a result of pelletization. Both of these discrete types of assemblages are intended to be encompassed herein by the term "granule".

In order to maximize the particle packing characteristics, the particle size distribution of the carbonate incorporated into the granule is in accordance with the equation

$$(1) \text{ Cumulative Percent finer than } D = \frac{(D^n - D_s^n)}{D_L^n - D_s^n} \times 100\%$$

where  $D$  = Particle size

$D_s$  = Smallest particle size - selected

$D_L$  = Largest particle size - selected

$n$  = Distribution modulus;

$D_L$  should be in the range of 100 to 1.0  $\mu\text{m}$ ;  $D_s$  in the range of 10 to 0.01  $\mu\text{m}$ ; and  $n$  is accorded a value appropriate for particles assumed to be approximately spherical. Preferably  $D_L$  is in the range of 44 to 2  $\mu\text{m}$ ,  $D_s$  is in the range of 0.5 to 0.1  $\mu\text{m}$ , and  $n$  is about 0.37. The carbonate used in the pellet may be an alkaline earth metal carbonate, such as a calcium carbonate, dolomite, magnesite or strontium carbonate, and is preferably a ground or chemically precipitated calcium carbonate or a mixture of ground and precipitated calcium carbonates. In many applications a ground marble is found to be particularly advantageous.

The method of producing desired particle sizes may be by comminution of naturally occurring carbonate minerals by a dry or a wet process, or by precipitation from an aqueous medium. They may be produced by blending of



components having different PSD's or from a production process which generates them naturally.

The thermoplastic granules of the invention are typically  
5 in the size range of from 5 to 10 mesh, and the end product thermoplastic with which the granules are to be blended may comprise granules in the same 5 to 10 mesh range.

10 The invention does not require the use of additional chemical materials for the purpose of preparation of the particulate product (the granules) or of re-dispersion of the particulate product in a thermoplastic composition, and thus the granules of the invention are preferably  
15 substantially free of a dispersing or fluidifacient additive. The granules may, however, include any additional functional additives which may be desired in the final thermoplastic formulation.

20 The hydrophobic material should be selected to render the surface of the inorganic material surface hydrophobic and compatible with organic polymers. Examples of such hydrophobic materials include carboxylic acids, or their salts, having from 3 to 20 carbon atoms in their  
25 hydrocarbon chain such as butyric, lauric, oleic and stearic acid, organosilane coupling agents, organotitanates and zircoaluminates. Other hydrophobic coating agents may be utilized.

30 Binders for use in the invention, preferably comprise an amorphous polyolefin or a highly branched polyethylene wax. Typical such binders are polypropylene homopolymers and amorphous copolymers of propylene and ethylene or butylene. It should be appreciated that the binders of  
35 the invention differ markedly from conventional prior art binders used in pellets of the present type. These conventional binders are typically polyolefins and

polyolefin waxes, which are thereby highly compatible with polyolefin polymers.

#### BRIEF DESCRIPTION OF DRAWINGS

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Figures 1 through 3 are graphs depicting particle size distributions for different ground calcium carbonate materials suitable for use in the invention, compared to values calculated by use of equation (1); and

10

Figure 4 is a graph comparing the PSD for a ground calcium carbonate not in accord with the invention, with the PSD for the ground product in Figure 3.

15

#### DESCRIPTION OF PREFERRED EMBODIMENTS

The invention will now be illustrated by a series of Examples, which should be considered as illustrative only and not delimitive of the invention otherwise set forth.

20

In the graphs of Figures 1 through 3, particle size distributions ("PSD's") for three different ground calcium carbonate products are shown, in comparison to the PSD calculated by use of equation (1). The ground calcium carbonate in each instance has a value of  $D_5$  and  $D_L$  as indicated in the Figure, and it will be evident that the said ground products very closely accord with the calculated curves. These ground products are appropriate for use with the present invention, and are used in the ensuing Examples.

30

The binders for the granules should be chemically and physically compatible with the host or matrix thermoplastic so that the resulting end product is not significantly weakened or discolored by the presence of the binder, and does not exhibit surface bloom from migration of the granule binder to the product surface.

35

Among the amorphous polyolefins utilizable as binders in the granules of the invention are amorphous polypropylene homopolymers. These differ from conventional polypropylenes which are highly crystalline.

5

The viscosities of useful such amorphous homopolymers (ASTM D3236) are in the range of 1000-2300 cps at 190°C. This translates to a theoretical Melt Flow Index of ca 90,000-40,000 g/10 minutes. Conventional polypropylene and polyethylene polymers have Melt Flow Indices in the range 200 down to 0.1.

Other less preferred grades of such homopolymers for use in the invention have a viscosity of 200 cps at 190°C (equivalent to 500,000 g/10 minutes MFI). A viscosity of 200 to 20,000 cps is preferred (equivalent to 500,000-5,000 g/10 minutes MFI); a viscosity of 500 to 5,000 cps is more preferred (equivalent to 200,000-15,000 g/10 minutes MFI); and a viscosity of 1,000 to 2,500 cps is most preferred (equivalent to 90,000-35,000 g/10 minutes MFI).

Amorphous copolymers of propylene and ethylene, and mixtures of copolymer with homopolymer are also effective for use in the invention.

The highly branched polyethylene waxes for use in the invention are preferably saturated, non-polar, synthetic hydrocarbon waxes which have been chemically neutralized. The special HULS/VEBA modification of the Ziegler low pressure polymerization of ethylene is typically used to produce the unique characteristics of this group of materials. The process confers branched-chain iso-paraffinic configurations.

35

The grade particularly preferred for use in the invention has a very high iso-paraffin (branched) configuration and

is predominantly branched chain. A typical such product has 70% branching, a molecular weight of 3,500 (by osmometry), an ASTM D-566 drop point at 102-110°C, density is 0.92, and a viscosity at 150°C of 300-380 cps.

5

#### EXAMPLE 1

Calcium carbonate with a  $D_L$  of 18 micrometers and a  $D_S$  of 0.35 micrometers (Figure 3) was treated with 1.0 percent  
10 of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 120 degrees celsius. This product was then placed in an internal mixer at a temperature of 160°C with an amorphous polypropylene homopolymer with a melting point of 152°C in the ratio of  
15 92:8 of treated calcium carbonate:polypropylene and was kneaded to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granules between 5 mesh and 10 mesh screens. The granulated product thus  
20 produced was blended with conventional polypropylene homopolymer with a melt flow index of 4.0 in the ratio of 88.9:11.1 polypropylene:granules. The blend was metered into a Kawaguchi reciprocating screw injection molding machine containing a screw with no mixing elements. The  
25 very high calcium carbonate-containing granules (92%  $\text{CaCO}_3$ ) dispersed readily into the blend and produced visually homogeneous molded parts.

#### EXAMPLE 2

30

Calcium carbonate with a  $D_L$  of 18 micrometers and a  $D_S$  of 0.35 micrometers (Figure 3) was treated with 1.0 percent of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 120°C. This product  
35 was then placed in an internal mixer at a temperature of 131°C with a highly branched polyethylene wax with a melting point of 121°C in the ratio of 92:8 of treated

calcium carbonate:polyethylene wax and was kneaded to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granules between 5 mesh and 10 mesh screens. The granulated product thus produced was blended with conventional polypropylene homopolymer with a melt flow index of 4.0 in the ratio of 88.9:11.1 polypropylene: granules. The blend was metered into a Kawaguchi reciprocating screw injection molding machine containing a screw with no mixing elements. The granules dispersed readily into the blend, and visually homogeneous calcium carbonate filled parts were molded.

### EXAMPLE 3

Calcium carbonate with a  $D_L$  of 18 micrometers and a  $D_S$  of 0.35 micrometers (Figure 3) was treated with 1.0 percent of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 150°C. This product was then placed in an internal mixer at a temperature of 160°C with polypropylene homopolymer in the ratio of 90:10 of treated calcium carbonate:polypropylene and was kneaded to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granules between 5 mesh and 10 mesh screens. The granulated product thus produced was blended with linear low density polyethylene with a melt flow index of 50 in the ratio of 88.9:11.1 polyethylene:granules. The blend was metered into an Arburg All-rounder 35 ton reciprocating screw injection molding machine containing a screw with no mixing elements. Homogeneous calcium carbonate filled parts were molded with the following properties (Table 1). It will be evident that the strength properties of the filled parts have not been substantially reduced. Optical properties are seen to be altered as a result of the addition of the calcium carbonate. The significance

of this depends on the contemplated end use.

Table 1

5		Unfilled	Filled
	Tensile strength (psi)	2045	1987
	Elongation at break (%)	350	340
10	Flexural strength (psi)	1441	1470
	Flexural modulus (psi x 100,000)	0.29	0.30
15	Izod impact strength (ft. lb/in) Notched Unnotched	no break no break	2.3 no break
	Gardner impact strength (ft. lb)	119	100
20	GE Brightness	32.8	52.5
	Hunter L	53.8	73.2
	Hunter a	-0.71	-1.13
	Hunter b	-5.20	1.18

25

EXAMPLE 4

Calcium carbonate with a  $D_L$  of 18 micrometers and a  $D_S$  of 0.35 micrometers (Figure 3) was treated with 1.0 percent of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 150°C. This product was then mixed using a two roll mill at a temperature of 160°C with a highly branched polyethylene wax in the ratio of 90:10 of treated calcium carbonate:wax to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granulate between 5 mesh and 10 mesh screens. The granulated product thus produced was

blended with high density polyethylene with a melt flow index of 30 in the ratio of 88.9:11.1 polyethylene:granules. The blend was metered into an Arburg All-rounder 35 ton reciprocating screw injection molding machine containing a screw with no mixing elements. Homogeneous calcium carbonate filled parts were molded with the following properties (Table 2)

Table 2

10

	Unfilled	Filled
Tensile strength (psi)	4136	3457
Elongation at break (%)	74	47
Flexural strength (psi)	5575	5174
Flexural modulus (psi x 100,000)	2.01	1.96
Izod impact strength (ft. lb/in) Notched Unnotched	1.5 no break	1.0 17.9
Gardner impact strength (ft. lb)	264	120
GE Brightness	47.0	58.6
Hunter L	67.1	77.2
Hunter a	-1.81	-1.71
Hunter b	-1.78	1.18

30

EXAMPLE 5

A ground calcium carbonate with a  $D_L$  of 3.8 micrometers and a  $D_S$  of 0.2 micrometers (Figure 1) was treated with 1.2 percent of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 150°C. This product was then mixed using a two roll mill at a

temperature of 162°C with an amorphous polypropylene wax with a melting point of 152°C in the ratio of 85:15 of treated calcium carbonate:amorphous polypropylene to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granulate between 5 mesh and 10 mesh screens. The granulated product thus produced was blended with a conventional polypropylene homopolymer with a melt flow index of 4 in the ratios of 88.2:11.8, 76.5:23.5 and 64.7:35.3 of polypropylene:granules to give calcium carbonate loadings of 10, 20 and 30 weight percents respectively. The blends were metered into an Arburg All-rounder 35 ton reciprocating screw injection molding machine containing a screw with no mixing elements. Homogeneous calcium carbonate filled parts were molded with the following properties (Table 3)

Table 3

	Unfilled	10%	20%	30%
Tensile strength (psi)	5077	4482	4154	3854
Elongation at break (%)	33	57	51	58
Flexural strength (psi)	6248	6245	6323	5949
Flexural modulus (psi x 100,000)	2.17	2.57	2.75	2.98
Izod impact strength (ft.lb/in)				
Notched	0.55	0.82	0.77	0.89
Unnotched	26.6	25.3	26.2	24.9
Gardner impact strength (ft.lb)	46	34	40	42
GE Brightness	15.7	61.1	63.4	63.4
Hunter L	35.0	79.0	81.8	82.1
Hunter a	-0.46	-1.00	-0.71	-0.58
Hunter b	-7.13	1.22	3.19	3.58



EXAMPLE 6

Calcium carbonate with a  $D_L$  of 6.5 micrometers and a  $D_S$  of 0.2 micrometers (Figure 2) was treated with 1.2 percent  
5 of stearic acid in a high speed mixer running at 4000 rpm for 5 minutes at a temperature of 150°C. This product was then mixed using a two roll mill at a temperature of 130°C with polyethylene wax with a melting point of 120°C in the ratio of 85:15 of treated calcium carbonate:  
10 polyethylene to form a homogeneous mixture. The resultant mixture was formed into granules by passing through a granulator and screening the resultant granulate between 5 mesh and 10 mesh screens. The granulated product thus produced was blended with  
15 polypropylene homopolymer with a melt flow index of 4 in the ratios of 88.2:11.8, 76.5:23.5 and 64.7:35.3 of polypropylene:granules to give calcium carbonate loadings of 10, 20 and 30 weight percents respectively. The blends were metered into an Arburg All-rounder 35 ton  
20 reciprocating screw injection molding machine containing a screw with no mixing elements. Homogeneous calcium carbonate filled parts were molded with the following properties (Table 4)

Table 4

	Unfilled	10%	20%	30%
5 Tensile strength (psi)	5040	4594	4188	3882
Elongation at break (%)	32	46	47	55
Flexural strength (psi)	6389	6375	6438	6381
10 Flexural modulus (psi x 100,000)	2.15	2.59	2.93	3.17
Izod impact strength (ft.lb/in)				
15     Notched	0.74	0.77	0.89	0.79
Unnotched	27.4	24.2	24.3	24.1
Gardner impact strength (ft.lb)	24	46	32	54
GE Brightness	18.8	60.5	63.6	64.0
Hunter L	38.9	78.4	81.7	82.5
20 Hunter a	-0.50	-0.89	-0.64	-0.41
Hunter b	-6.90	0.93	2.88	3.58

In the above Examples, tensile strength and elongation at break were measured by the procedure laid down in ASTM Standard No. D638, flexural strength and flexural modulus by the procedure laid down in ASTM Standard No. D790, Izod impact strength by the procedure laid down in ASTM Standard No. D256, and Gardner impact strength by the procedure laid down in ASTM Standard No. D3029 method G, and GE brightness by the procedure laid down in TAPPI Standard No. T646om86.

The color of the thermoplastic compositions was measured, using a disc as a test piece, by a system which is based on the formula known as the Hunter L a b formula using an illuminant C light source. Five measurements of the light were made using a Technidyne spectrophotometer to determine the tristimulus values X, Y and Z. L, a and b values were calculated according to the formulae:

$$L = 100(Y/Y_0)^{1/2}$$

$$a = K_a(X/X_0 - Y/Y_0)/(Y/Y_0)^{1/2}$$

$$b = K_b(Y/Y_0 - Z/Z_0)/(Y/Y_0)^{1/2}$$

5        where  $K_a$  and  $K_b$  are the chromaticity coefficients.  
and  $X_0$ ,  $Y_0$ ,  $Z_0$  are tristimulus values for a perfect  
diffuser.

For illuminant C  $K_a=175$ ,  $K_b=70$ ,  $X_0=98.041$ ,  $Y_0=100.000$ ,  
10  $Z_0=118.103$

The  $L$  value can be said to represent the lightness or  
darkness of shade, while the  $a$  and  $b$  values can be said  
to be coordinates representing chromaticity ( $-a$  = green,  
15  $+a$  = red,  $-b$  = blue and  $+b$  = yellow).

#### EXAMPLE 7

A series of samples of granules were prepared by the  
20 method of Example 1, using different loading levels of  
calcium carbonate. The carbonate was of two types -- (1)  
the carbonate of Example 1; and (2) control ground marble  
having a PSD not conforming to Equation (1), but having a  
median particle size the same as the carbonate used in  
25 Example 1. Figure 4 depicts the PSD for the ground  
carbonate (2) which is not in accord for use in the  
invention, and compares this with the PSD for the ground  
product (1) of Example 1. The scale used in Figure 4 is  
linear (Figures 1 to 3 employ a logarithmic scale for the  
30 abscissa) in order to clearly show the differences in the  
respective PSD's. Two different binders were used, viz.  
a conventional binder, i.e. a conventional paraffin wax,  
and an amorphous polypropylene of the type used in  
Example 1. The % solids content of the granule above  
35 which dispersion does not occur in polypropylene was  
determined by visually examining the resultant specimens  
for undispersed agglomerates. The results were as

follows:

Table 5

5     % SOLIDS CONTENT OF THE GRANULE, ABOVE WHICH DISPERSION  
         IN POLYPROPYLENE DOES NOT OCCUR

	Conventional Binder	Binder of Invention
10     Control Carbonate	below 80%	87%
Carbonate of Example 1	below 80%	90-92%

While the present invention has been particularly set  
15 forth in terms of specific embodiments thereof, it will  
be understood in view of the instant disclosure, that  
numerous variations upon the invention are now enabled to  
those skilled in the art, which variations yet reside  
within the scope of the present teaching. Accordingly,  
20 the invention is to be broadly construed, and limited  
only by the scope and spirit of the claims now appended  
hereto.

WHAT IS CLAIMED IS:

1        1. A thermoplastic granule containing a high  
2        proportion of a particulate carbonate filler in a  
3        thermoplastic binder, for blending with an end product  
4        thermoplastic in which the carbonate filler is to be  
5        dispersed; comprising:

7                   at least 85% by weight of a particulate  
8 carbonate which is coated with one or more fatty acids  
9 having a carbon chain length of from 12 to 20 carbon  
10 atoms;

the balance of said granule by weight being a thermoplastic polymeric binder which is solid at ambient temperature and is compatible with said end product thermoplastic in which said carbonate filler is to be dispersed, said polymeric binder being selected from one or more members of the group consisting of amorphous polyolefins and highly branched polyethylene waxes.

1           2. A thermoplastic granule in accordance with claim  
2   1, in which the particle size distribution of said  
3   carbonate is in accordance with the equation

$$\text{Cumulative Percent finer than D} = \frac{(D^0 - D_s^n)}{D_1^n - D_s^n} \times 100\%$$

```

9   where D  = Particle size
10         Ds = Smallest particle size
11         DL = Largest particle size
12         n   = Distribution modulus

```

1           3. A thermoplastic granule in accordance with claim  
2 2 in which  $D_L$  is in the range of 100 to 1.0  $\mu\text{m}$ ;  $D_s$  is in  
3 the range of 10 to 0.01  $\mu\text{m}$ ; and  $n$  has a value appropriate  
4 for carbonate particles assumed to be approximately

5 spherical.

1           4. A thermoplastic granule in accordance with claim  
2 3, in which  $D_L$  is in the range of 44 to 2  $\mu\text{m}$ ,  $D_s$  is in the  
3 range of 0.5 to 0.1  $\mu\text{m}$ , and  $n$  is about 0.37.

1           5. A thermoplastic granule in accordance with claim  
2 2, wherein said carbonate is an alkaline earth metal  
3 carbonate.

1           6. A thermoplastic granule in accordance with claim  
2 5, wherein said carbonate is a ground carbonate.

1           7. A thermoplastic granule in accordance with claim  
2 6, wherein said carbonate is a ground marble.

1           8. A thermoplastic granule in accordance with claim  
2 5, wherein said carbonate comprises a chemically  
3 precipitated calcium carbonate.

1           9. A thermoplastic granule in accordance with claim  
2 5, wherein said carbonate is a mixture of ground and  
3 precipitated calcium carbonates.

1           10. A thermoplastic granule in accordance with  
2 claim 5, in which said granule is the size range of from  
3 5 to 10 mesh, and wherein said end product thermoplastic  
4 with which said granule is to be blended comprises  
5 granules in said 5 to 10 mesh range.

1           11. A thermoplastic granule in accordance with  
2 claim 2, in which said particulate carbonate is present  
3 in the range of 85 to 92% by weight.

1           12. A thermoplastic granule in accordance with  
2 claim 1, in which said binder comprises an amorphous  
3 polypropylene homopolymer.

1        13. A thermoplastic granule in accordance with  
2 claim 2, in which said binder comprises an amorphous  
3 polypropylene homopolymer.

1        14. A thermoplastic granule in accordance with  
2 claim 1, in which said binder comprises an amorphous  
3 copolymer of propylene and ethylene.

1        15. A thermoplastic granule in accordance with  
2 claim 2, in which said binder comprises an amorphous  
3 copolymer of propylene and ethylene.

1        16. A thermoplastic granule in accordance with  
2 claim 1, in which said binder comprises an amorphous  
3 copolymer of propylene and butylene.

1        17. A thermoplastic granule in accordance with  
2 claim 2, in which said binder comprises an amorphous  
3 copolymer of propylene and butylene.

1        18. A thermoplastic granule in accordance with  
2 claim 1, in which said binder comprises a saturated, non-  
3 polar, synthetic hydrocarbon wax which has been  
4 chemically neutralized and is predominantly branched  
5 chain.

1        19. A thermoplastic granule in accordance with  
2 claim 2, in which said binder comprises a saturated, non-  
3 polar, synthetic hydrocarbon wax which has been  
4 chemically neutralized and is predominantly branched  
5 chain.

1        20. A method for preparing a thermoplastic end  
2 product in which a carbonate filler is dispersed;  
3 comprising:  
4

5 preparing thermoplastic granules containing a  
6 high proportion of a particulate carbonate filler in a  
7 thermoplastic binder, for blending with the end product  
8 thermoplastic in which the carbonate filler is to be  
9 dispersed; said granules comprising at least 85% by  
10 weight of a particulate carbonate which is coated with  
11 one or more fatty acids having a carbon chain length of  
12 from 12 to 20 carbon atoms; the balance of said granules  
13 by weight being a thermoplastic polymeric binder which is  
14 solid at ambient temperature and is compatible with said  
15 end product thermoplastic in which said carbonate filler  
16 is to be dispersed, said polymeric binder being selected  
17 from one or more members of the group consisting of  
18 amorphous polyolefins and highly branched polyethylene  
19 waxes;

20

21 blending said granules with said end product  
22 thermoplastic to achieve the desired loading with said  
23 filler; and

24

25 forming the resulting blend into the shape of  
26 said end product.

1 21. The method of claim 20 in which the particle  
2 size distribution of said carbonate in said granules is  
3 in accordance with the equation

4

5 Cumulative Percent finer than D =  $(D^n - D_s^n) \times 100\%$

6

7

8

$$\frac{D_L^n - D_s^n}{D_L^n - D_s^n}$$

9 where D = Particle size

10  $D_s$  = Smallest particle size

11  $D_L$  = Largest particle size

12 n = Distribution modulus

1 22. The method of claim 21 in which  $D_L$  is in the  
2 range of 100 to 1.0  $\mu\text{m}$ ;  $D_s$  is in the range of 10 to 0.01



3  $\mu\text{m}$ ; and n has a value appropriate for carbonate particles  
4 assumed to be approximately spherical.

1 23. The method of claim 22, in which  $D_L$  is in the  
2 range of 44 to 2  $\mu\text{m}$ ,  $D_s$  is in the range of 0.5 to 0.1  $\mu\text{m}$ ,  
3 and n is about 0.37.

1 24. The method of claim 20, in which the binder of  
2 said thermoplastic granules comprises an amorphous  
3 polypropylene homopolymer.

1 25. The method of claim 20, in which said binder  
2 for said granules comprises an amorphous polypropylene  
3 homopolymer.

1 26. The method of claim 20, in which said binder  
2 for said granules comprises a saturated, non-polar,  
3 synthetic hydrocarbon wax which has been chemically  
4 neutralized and is predominantly branched chain.

1 27. The method of claim 21, in which said binder  
2 for said granules comprises a saturated, non-polar,  
3 synthetic hydrocarbon wax which has been chemically  
4 neutralized and is predominantly branched chain.

1 28. A method for preparing a carbonate filled  
2 molded thermoplastic end product, comprising:

3  
4 blending the thermoplastic material which is to  
5 be filled with said carbonate with thermoplastic granules  
6 containing a high proportion of a particulate carbonate  
7 filler in a thermoplastic binder to disperse said  
8 carbonate in the thermoplastic material to be filled at a  
9 desired loading; said granules comprising at least 85% by  
10 weight of a particulate carbonate which is coated with  
11 one or more fatty acids having a carbon chain length of  
12 from 12 to 20 carbon atoms; the balance of said granules

13 by weight being a thermoplastic polymeric binder which is  
14 solid at ambient temperature and is compatible with said  
15 end product thermoplastic in which said carbonate filler  
16 is to be dispersed, said polymeric binder being selected  
17 from one or more members of the group consisting of  
18 amorphous polyolefins and highly branched polyethylene  
19 waxes; and molding the resultant blend into the shape of  
20 said end product.

1 29. A method in accordance with claim 28, in which  
2 the particle size distribution of said carbonate is in  
3 accordance with the equation

4  
5 Cumulative Percent finer than D =  $\frac{(D^n - D_s^n)}{D_L^n - D_s^n} \times 100\%$   
6  
7  
8

9 where D = Particle size  
10  $D_s$  = Smallest particle size  
11  $D_L$  = Largest particle size  
12 n = Distribution modulus

1 30. A thermoplastic granule containing a high  
2 proportion of a particulate carbonate filler in a  
3 thermoplastic binder, comprising:

4  
5 at least 85% by weight of a particulate  
6 carbonate which is coated with one or more fatty acids  
7 having a carbon chain length of from 12 to 20 carbon  
8 atoms;

9  
10 the balance of said granule by weight being a  
11 thermoplastic polymeric binder which is solid at ambient  
12 temperature, said polymeric binder being selected from  
13 one or more members of the group consisting of amorphous  
14 polyolefins and highly branched polyethylene waxes.

1 31. A thermoplastic granule in accordance with

2 claim 30, in which the particle size distribution of said  
3 carbonate is in accordance with the equation

4

5 Cumulative Percent finer than  $D = (D^n - D_s^n) \times 100\%$

6

7

$$\frac{D_L^n - D_s^n}{D_L^n - D_s^n}$$

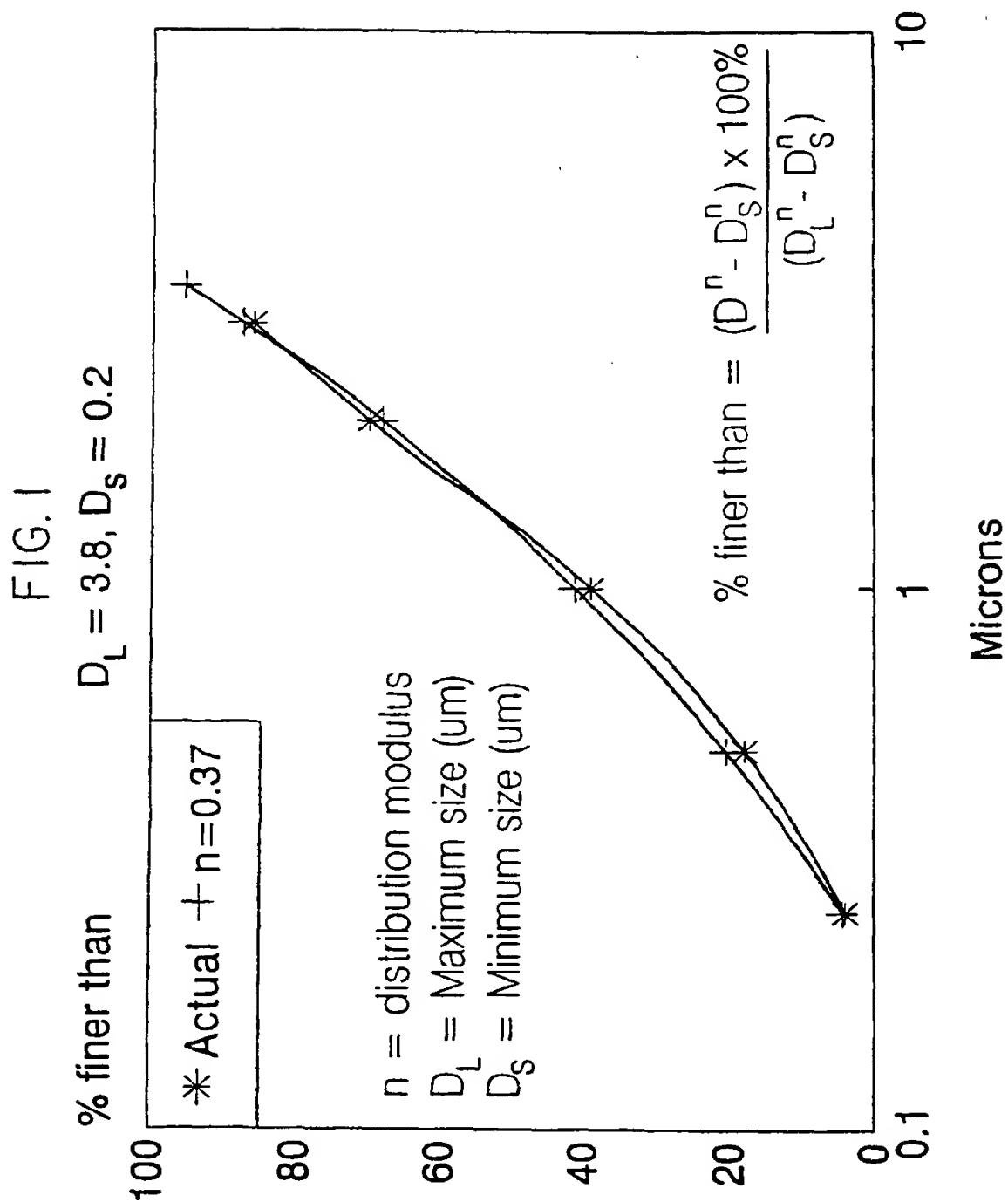
8 where  $D$  = Particle size

9  $D_s$  = Smallest particle size

10  $D_L$  = Largest particle size

11  $n$  = Distribution modulus

1 / 4



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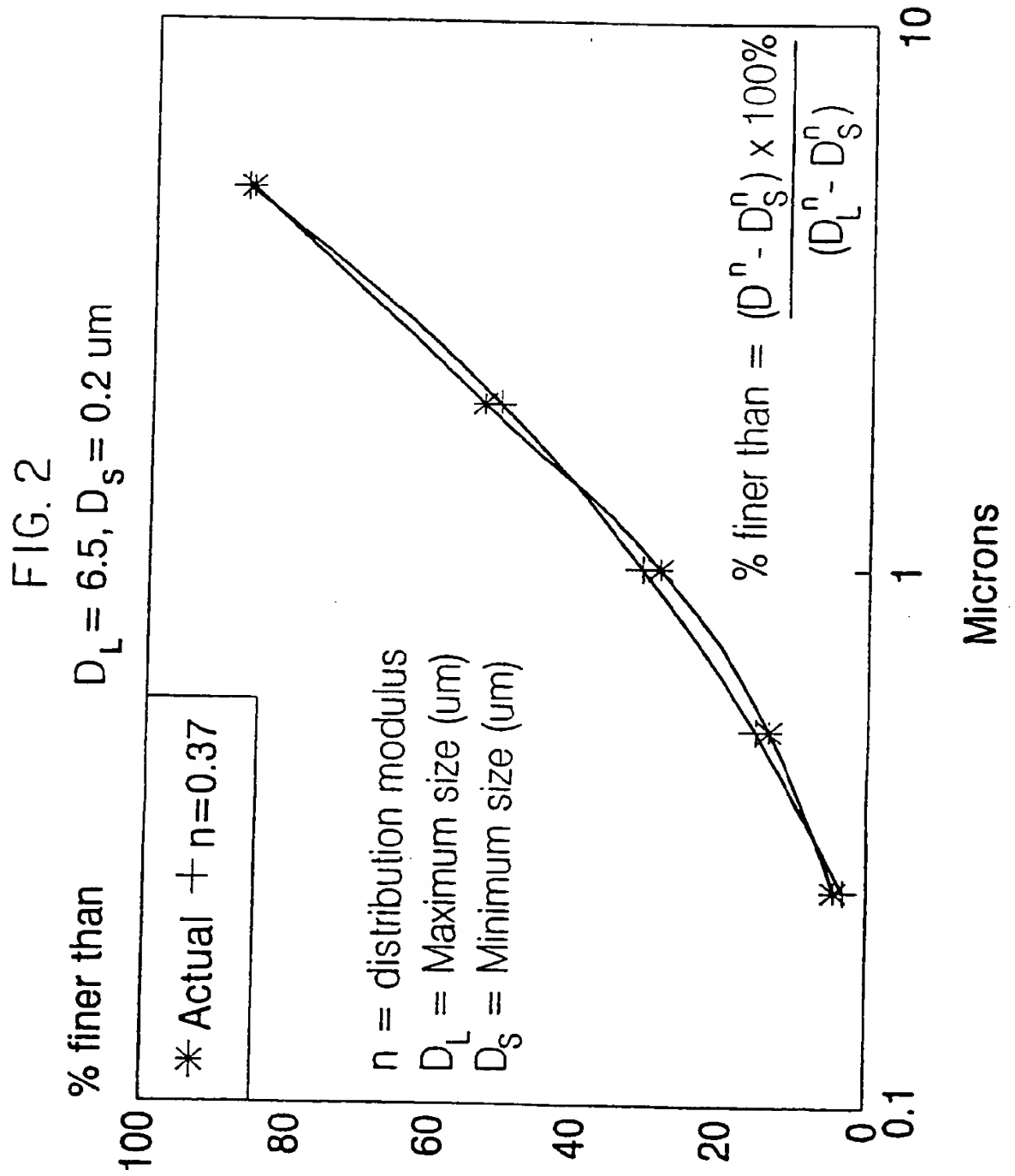
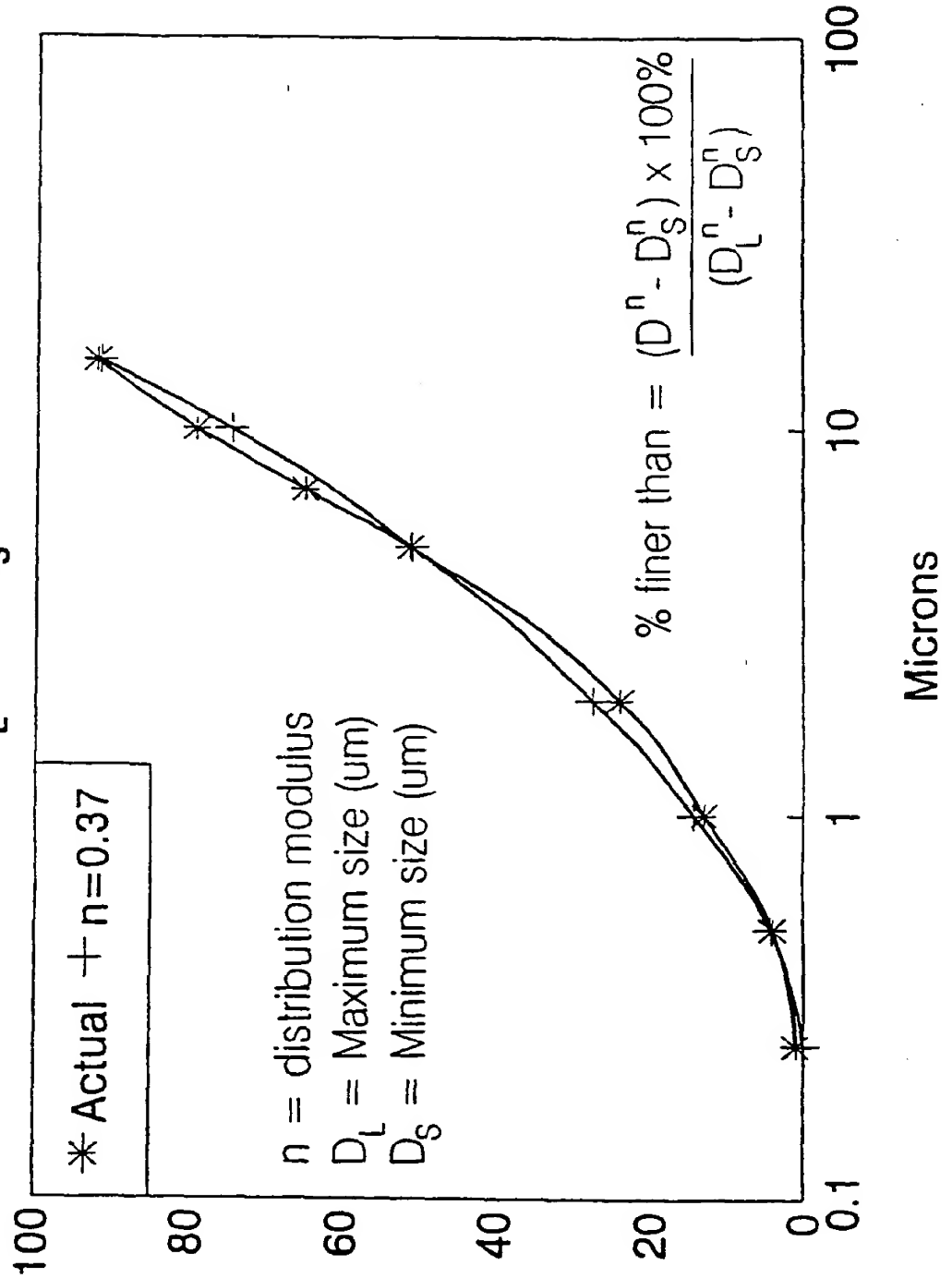


FIG. 3

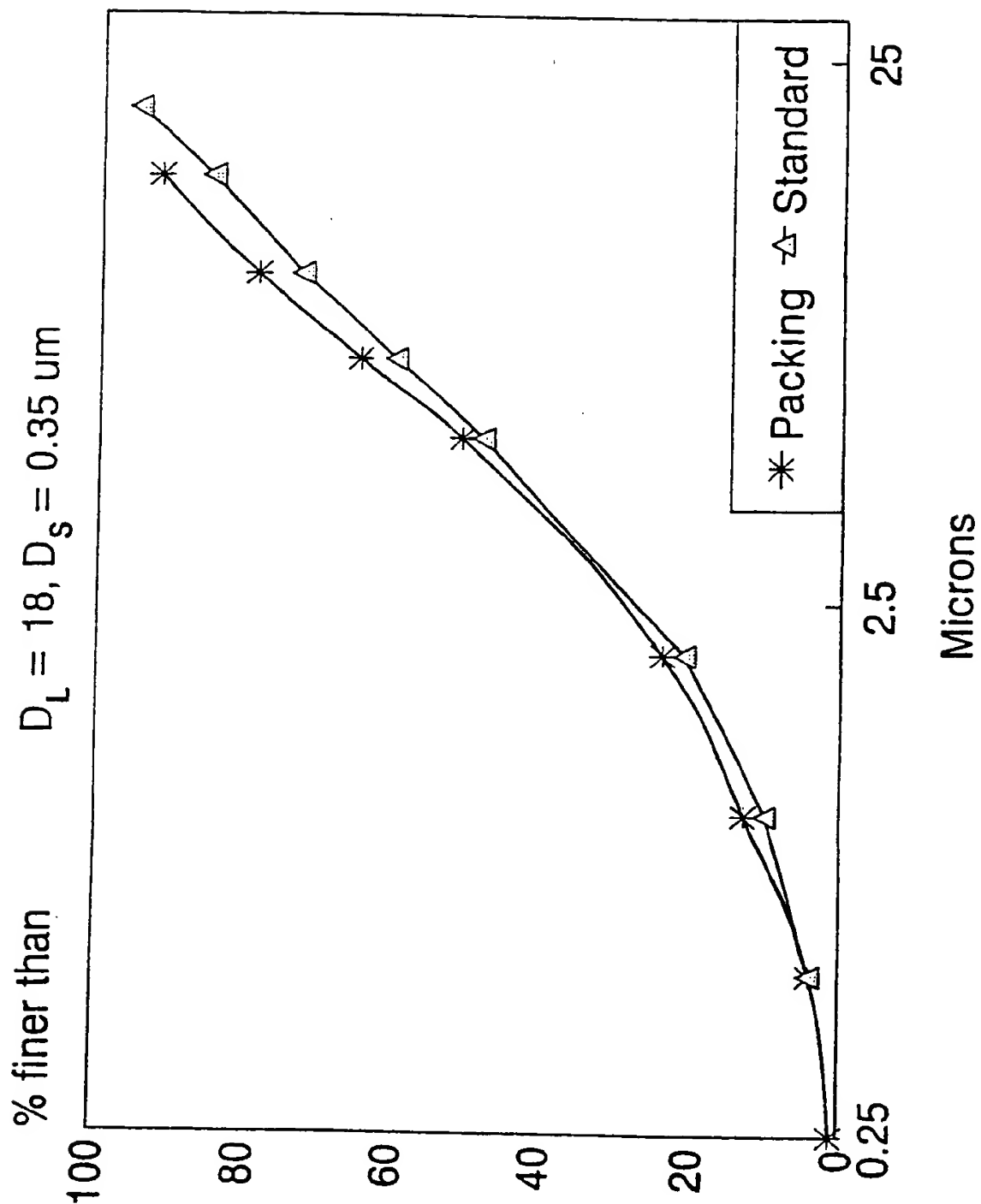
$D_L = 18, D_S = 0.35 \text{ } \mu\text{m}$

% finer than



4 / 4

FIG. 4

 $D_L = 18, D_S = 0.35 \mu\text{m}$ 

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/14400

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 10/00, 12/00; C08K 3/00; C04B 18/02  
US CL : 524/425

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/425

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA, A, 2,016,447 (PLUSS-STAUER AG) 11 November 1990, pages 2-3 and 9-11, all lines.	1-31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 FEBRUARY 1995

Date of mailing of the international search report

03 APR 1995

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